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## Selective Permeability of PVA Membranes. I. Radiation-Crosslinked Membranes

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### Synopsis

The water and salt transport properties of ionizing radiation crosslinked poly(vinyl alcohol) (PVA) membranes were investigated. The studied membranes showed high permeabilities and low selectivities for both water and salt. The results were found to be in accord with a modified solution-diffusion model for transport across the membranes, in which pressure-dependent permeability coefficients are employed.

### INTRODUCTION

Since the discovery of the Loeb-Sourirajan-type modified cellulose acetate (CA) reverse osmosis (RO) membranes,<sup>1</sup> considerable research efforts have been dedicated to the development of new types of RO membranes. Different materials have been investigated to overcome certain limitations of the cellulosic membranes. Poly(vinyl alcohol) (PVA) is known as a good film-forming, highly hydrophilic polymer and, as such, has also been considered for RO studies. Michelsen and Harriot<sup>2</sup> investigated the RO characteristics of untreated PVA membranes, but the data reported by them showed rather poor RO performance. Several attempts to improve the RO characteristics of PVA membranes by various treatments have been reported in the literature.<sup>3-5</sup> In some of these studies the PVA was crosslinked by chemical methods and, in all cases, the RO performance of the resulting membranes was found to be considerably improved in comparison with the untreated PVA.

The primary objective of this work was to investigate the effect of radiation crosslinking on the transport properties of PVA membranes and, in particular, on the water and salt permeability of these membranes.

### EXPERIMENTAL

#### Materials

Two grades of PVA supplied by Aldrich Chemical Co. were tested: (a) 100% hydrolyzed, 86,000 MW, and (b) 100% hydrolyzed, 115,000 MW. Samples made of 86,000 MW material were designated by the prefix 80, while samples made of the other material were designated by the prefix 90 (see Table I).

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TABLE I  
Composition and Preparation Conditions of PVA Membranes Used in the Permeability Tests

Membrane	PVA		Thickness, $\mu\text{m}$	Irradiation dose, Mrad
	% Hydrolyzed	MW		
80 GF 2	100	86,000	4.1	14.0
80 GF 51	100	86,000	3.8	28.0
80 GF 52	100	86,000	4.0	28.0
90 GF 2	100	115,000	3.8	14.0
90 GF 51	100	115,000	4.1	28.0
90 GF 52	100	115,000	4.0	28.0

### Film Casting

The PVA films were cast from 8–10 wt % aqueous solutions between two polyethylene sheets, using a Gardner knife and subsequently drying in air, at room temperature, in a dust-free laminar flow hood. The use of the polyethylene sheets contributed to the ease of handling and reproducibility of the prepared membranes. Film thicknesses in the range 3–20  $\mu\text{m}$  were obtained by this technique. The dry film thickness was determined by a step-height measurement using a Taylor–Hobson model 3 Talysurf, as well as by weighing films of known areas and using the separately determined density of dry PVA of 1.30  $\text{g}/\text{cm}^3$ . The thicknesses determined by these two methods agreed within  $\pm 5\%$ .

### Radiation Crosslinking

Irradiation of aqueous solutions of PVA to obtain crosslinked, water-insoluble hydrogels is a well-known and documented technique.<sup>6,7</sup> Irradiation has been shown to be also useful for crosslinking water-swollen PVA films.<sup>8,9</sup> The membrane samples (5 cm in diam and 16–18  $\mu\text{m}$  thick) were immersed in an aqueous solution of 40% methanol (by volume) and left to equilibrate for 24 h. Nitrogen gas was bubbled through the solutions to eliminate dissolved oxygen. At the end of this treatment, the sample containers were sealed and irradiated at room temperature with doses in the range 0.5–40 Mrad, at a dose rate of 153 krad/h, in a Gammacell 220, cobalt-60 irradiation unit supplied by Atomic Energy of Canada, Ltd.

The irradiated samples were transferred to a bath filled with distilled water and left to equilibrate. Their diameter,  $D(\text{H}_2\text{O})$ , in the swollen state was measured with a ruler. The  $D(\text{H}_2\text{O})$  values obtained for different irradiation doses are plotted in Figure 1. The swollen samples were removed from the distilled water, blotted dry with lens paper, and weighed to determine the swollen weight. The ratio between the water-swollen weight and the dry weight of the membrane, defined as the swelling ratio, is plotted vs. the irradiation dose (Fig. 2). Sol–gel fractions were determined by enclosing the samples in stainless steel “cages” and placing the cages for 2–4 h in boiling distilled water, followed by drying in air at room temperature, and weighing. The percent sol is plotted vs. irradiation dose in Figure 3. Extrapolation of the log (sol %) vs. log (dose) plot to 100% sol yields the incipient gelation dose. As can be seen in Figure 3, the incipient gelation dose for the two samples is in the range 7–10 Mrad, which is within the range 5–20 Mrad reported by Ikada and Mita<sup>8</sup> for electron beam-treated, water-swollen PVA membranes.

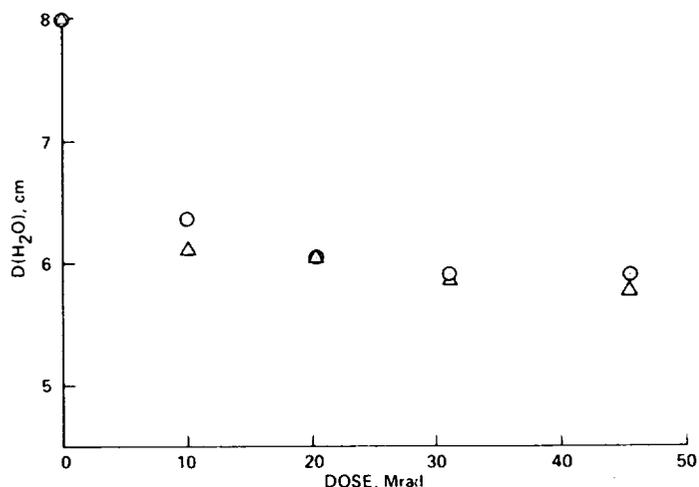


Fig. 1. Water-swollen diameters of samples irradiated with various doses:  $\Delta$ , 90 GF 50;  $\circ$ , 80 GF 50. (The dry diameter of the samples was 5.08 cm.)

The plots of  $D(\text{H}_2\text{O})$  and swelling ratio vs. irradiation dose in Figures 1 and 2 indicate a steep decrease in these parameters with dose in the range below 10 Mrad; beyond 10 Mrad, they change only slightly with dose. Therefore, the membranes chosen for permeability measurements were irradiated to doses

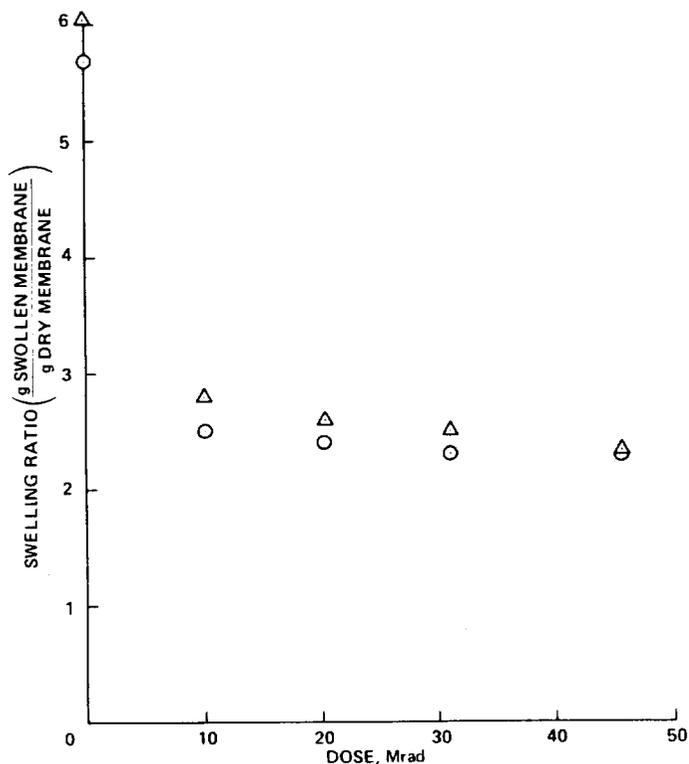


Fig. 2. Swelling ratio in water of samples irradiated with various doses:  $\Delta$ , 90 GF 50;  $\circ$ , 80 GF 50.

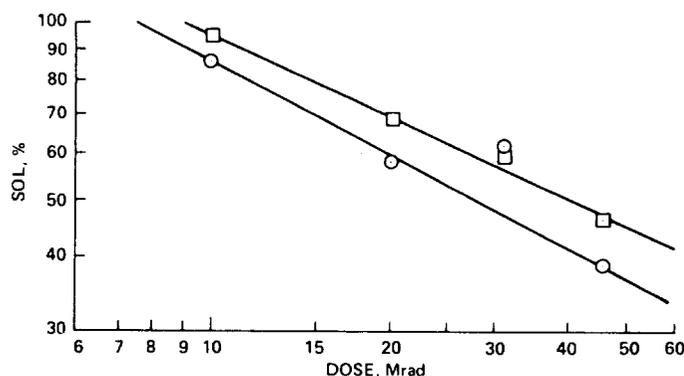


Fig. 3. Dependence of sol fraction on radiation dose: ○, 90 GF 50; □, 80 GF 50.

greater than 10 Mrad. Table I summarizes the composition and preparation conditions of the membranes used in the permeability tests.

### Permeability Testing

The irradiated membranes were tested for water flux and salt rejections using a recirculating hyperfiltration system similar to the one described previously.<sup>10</sup> Tested membranes were backed with MF-Millipore-VM microporous filters and supported by a 5- $\mu$ m porous stainless steel disc. The average linear feed flow velocity over the membrane surface during RO testing was maintained in the range 40–50 cm/s. Salt rejections were not influenced significantly by reducing the feed flow velocity to 30 cm/s. The higher flow velocity range was employed in this work to minimize concentration polarization. The membranes were tested at various feed concentrations and pressures (up to 1000 psi) in a temperature range between 25 and 70°C.

The salt concentrations of the feed and product streams were measured conductometrically using a CDC 334 thermostated flowthrough conductivity cell made by Radiometer—Copenhagen. Product water flux was determined volumetrically by flowing the product stream through calibrated micropipets during the measurement.

## RESULTS

The solution-diffusion model developed by Lonsdale<sup>11</sup> was employed in the analysis of the material transport through the homogeneous PVA membranes. According to this model, the water flux ( $F_w$ ), the salt flux ( $F_s$ ), and the salt rejection ( $R_s$ ) of a membrane are given by the following equations:

$$F_w = -\frac{D_{wm}C_{wm}\bar{V}_w(\Delta P - \Delta\pi)}{RT\lambda} = -\frac{P_w\bar{V}_w(\Delta P - \Delta\pi)}{RT\lambda} \quad (1)$$

$$F_s = -D_{sm}K\frac{\Delta C_s}{\lambda} = -\frac{P_s\Delta C_s}{\lambda} \quad (2)$$

$$R_s = \frac{\Delta C_s}{C'_w} = \left(1 + \frac{P_s}{P_w}\frac{RTC'_w}{\bar{V}_w(\Delta P - \Delta\pi)}\right)^{-1} \quad (3)$$

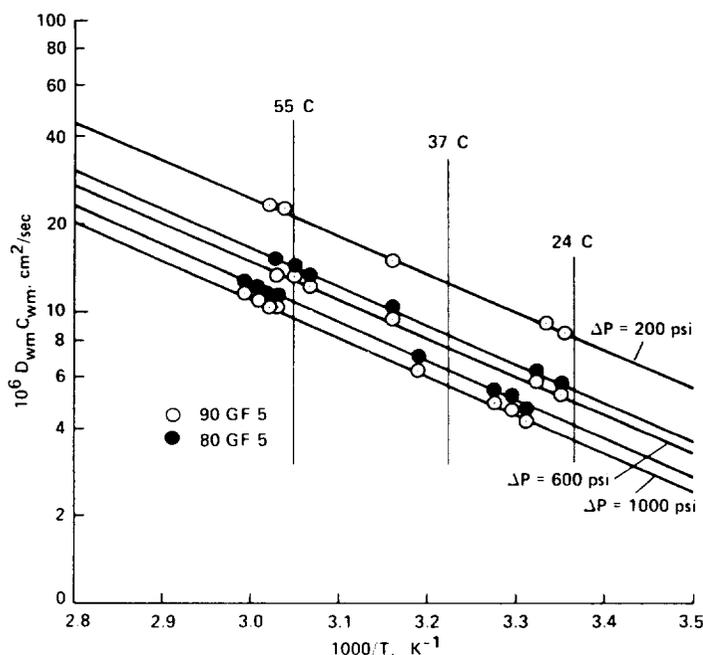


Fig. 4. Temperature dependence of the water permeability of radiation-crosslinked PVA membranes under various pressure differentials: O, 90 GF 5; ●, 80 GF 5. (The lines are the best fit to the data points evaluated by linear regression analysis.)

where  $D_{wm}$  is water diffusion coefficient,  $\text{cm}^2/\text{s}$ ;  $C_{wm}$  is equilibrium water content of the swollen membrane,  $\text{g}/\text{cm}^3$ ;  $\bar{V}_w$  is partial molar volume of water in the membrane,  $\text{cm}^3/\text{mol}$ ;  $R$  is gas constant;  $T$  is absolute temperature,  $\text{K}$ ;  $\Delta P$  is hydrostatic pressure drop across the membrane,  $\text{psi}$ ;  $\Delta\pi$  is osmotic pressure drop across the membrane,  $\text{psi}$ ;  $\lambda$  is effective membrane thickness,  $\text{cm}$ ;  $P_w = D_{wm}C_{wm}$  is water permeability coefficient,  $\text{cm}^2/\text{s}$ ;  $D_{sm}$  is salt diffusion coefficient,  $\text{cm}^2/\text{s}$ ;  $K$  is molar distribution coefficient,  $(\text{g salt}/\text{cm}^3 \text{ membrane})/(\text{g salt}/\text{cm}^3 \text{ solution})$ ;  $\Delta C_s$  is bulk solution concentration difference across the membrane,  $\text{g}/\text{cm}^3$ ;  $P_s$  is  $D_{sm}K =$  salt permeability coefficient,  $\text{cm}^2/\text{s}$ ; and  $C'_w, C''_w$  are concentrations on the high and low pressure sides of the membrane, respectively,  $\text{g}/\text{cm}^3$ .

The transport properties of PVA membranes crosslinked by irradiation to a dose of 28 Mrad are presented. Several tests performed on PVA membranes

TABLE II  
Activation Energies of the Water Permeability of PVA Membranes at Various Pressures

Pressure, psi	Activation energy, kcal/mol	
	80 GF 5	90 GF 5
0 <sup>a</sup>	6.03 ± 0.10	6.11 ± 0.10
200	6.00 ± 0.25	6.04 ± 0.18
600	—	6.03 ± 0.12
1000	—	6.03 ± 0.07
∞ <sup>b</sup>	6.16 ± 0.10	5.95 ± 0.10

<sup>a</sup> Calculated from the extrapolated value of  $(P_w)^{-1}$  at  $\Delta P = 0$ ; see eq. (4).

<sup>b</sup> Calculated from the extrapolated value of  $(P_w)^{-1}$  at very high pressures; see eq. (4).

crosslinked by irradiation to a dose of 14 Mrad indicated no significant effect of the irradiation dose, in this range, on the transport properties of the crosslinked PVA membranes.

The temperature dependence of the water permeability at different pressures is given in Figure 4. As shown, at each applied pressure, an Arrhenius-type dependence of  $P_w$  on temperature is observed. From this dependence the activation energies were evaluated by linear regression analysis of the data points and are listed in Table II.

The data in Figure 4 also indicate that, at constant temperature, the water permeability decreases with increasing applied pressure. A plot of the reciprocal of  $P_w$  vs. the pressure differential  $\Delta P$  across the membrane (under the experimental conditions employed here,  $\Delta\pi$  was always less than 10 psi and, hence, negligibly small) indicates a linear relationship between these parameters (Fig. 5).

While the salt concentration of the feed has no observable effect on the water

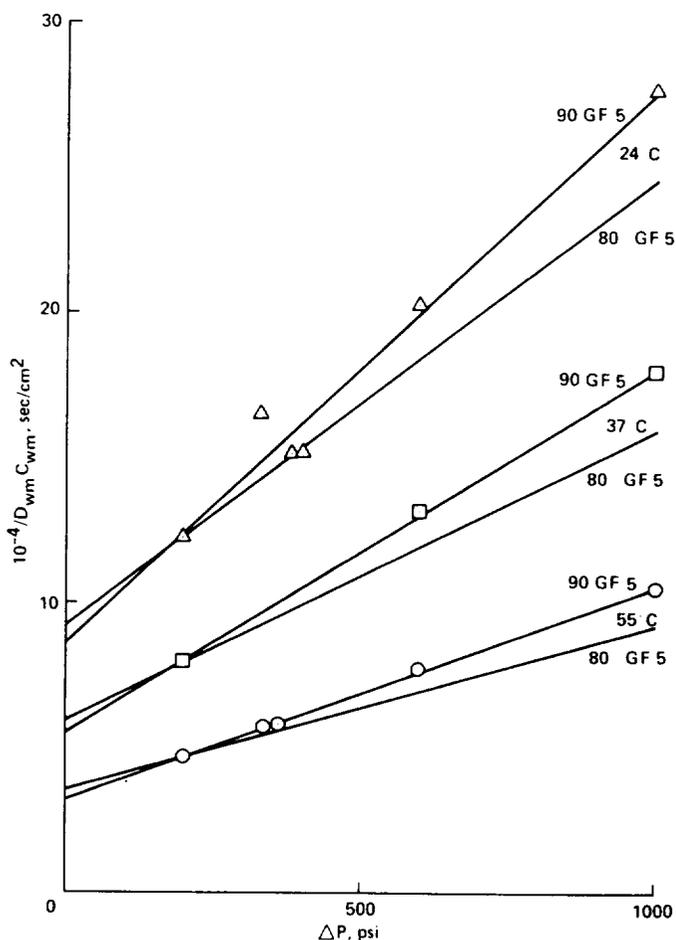


Fig. 5. Pressure dependence of the water permeability through radiation-crosslinked PVA at various temperatures. (The lines are the best fit to the data points evaluated by linear regression analysis.)

transport through the membrane, it has a very pronounced effect on the salt transport, as indicated by the strong dependence of the salt rejection  $R_s$  on the feed concentration shown in Figure 6. These graphs also indicate that for a given feed concentration, the salt rejection decreases with a decrease in applied pressure. Plots of  $(R_s)^{-1}$  vs.  $(\Delta P)^{-1}$  shown in Figure 7 indicate that the experimental data follow the linear correlation expressed by eq. (3), as expected for a solution-diffusion membrane.

The salt rejections of the studied PVA membranes were found to be virtually independent of temperature, indicating that the activation energy of salt permeation is the same in these membranes as the activation energy of water permeation.

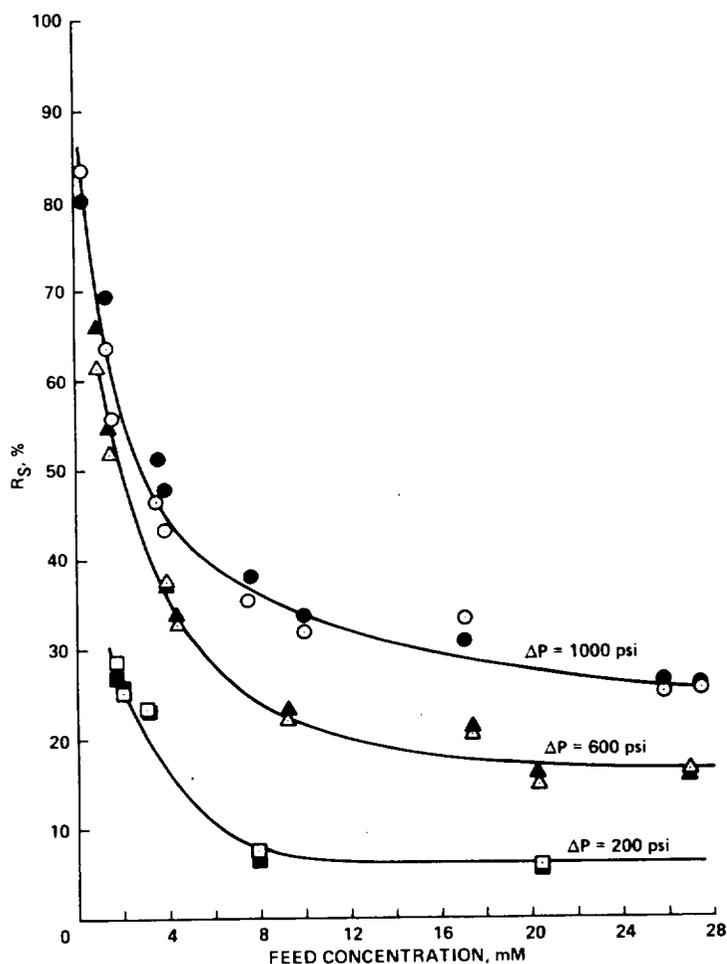


Fig. 6. Feed concentration dependence of the salt rejection of radiation-crosslinked PVA membranes under various pressure differentials:  $\circ$ ,  $\bullet$ — $\Delta P = 1000$  psi;  $\Delta$ ,  $\blacktriangle$ — $\Delta P = 600$  psi;  $\square$ ,  $\blacksquare$ — $\Delta P = 200$  psi (open symbol, 90 GF 5; filled, 80 GF 5).

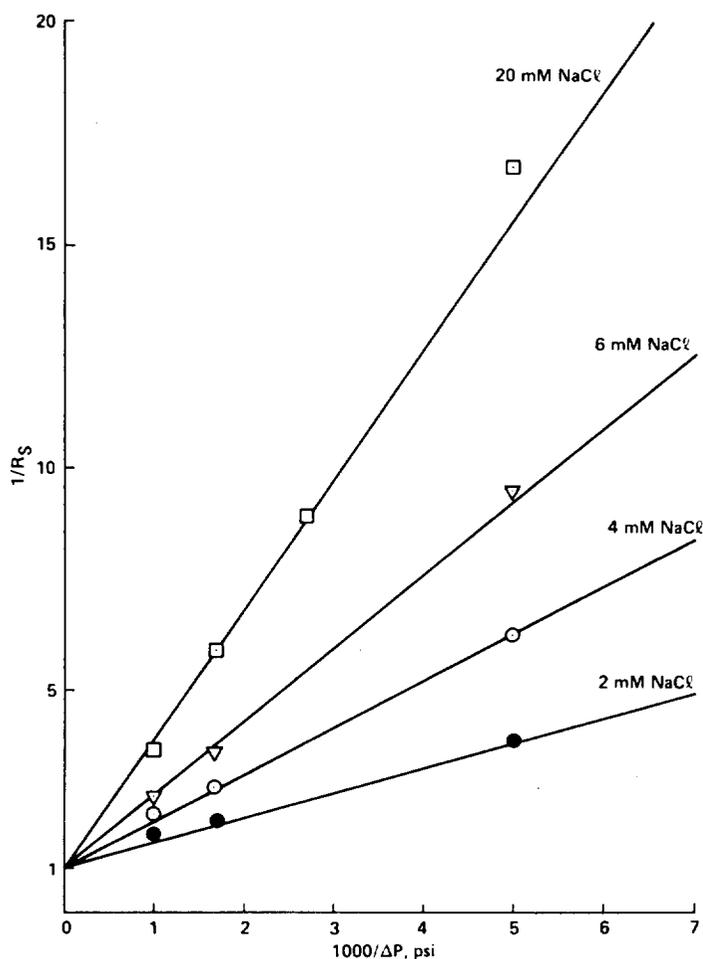


Fig. 7. Pressure dependence of the rejection at various feed concentrations.

### DISCUSSION

The water permeability coefficients ( $P_w$ ) through the radiation-crosslinked membranes were found to be in the range  $10^{-6}$ – $10^{-5}$   $\text{cm}^2/\text{s}$  using eq. (1) for their evaluation.

The pressure dependence of  $P_w$  as shown in Figures 4 and 5 requires some comment. While generally in conventional solution-diffusion membranes, such as cellulose acetate and polyamides, eq. (1) is observed with pressure-independent permeability coefficients (i.e., a linear dependence of  $F_w$  on  $\Delta P$ ), in swollen hydrogel membranes the dependence of the solvent flux on the pressure differential is nonlinear.<sup>12,13</sup> It may be argued that eq. (1) is still valid in the case of hydrogel membranes and that the nonlinearity of the  $F_w$  dependence on  $\Delta P$  is caused by the fact that the permeability coefficient  $P_w$  itself is pressure dependent. The linear correlation between the reciprocal water permeability and the pressure may be expressed by an equation of the form

$$\frac{1}{P_w} = \frac{1}{D_{wm}C_{wm}} = a + b \Delta P \quad (4)$$

where  $a$  represents the extrapolated value of  $(P_w)^{-1}$  to  $\Delta P = 0$  and  $b \Delta P$  represents the value of  $(P_w)^{-1}$  at very high pressures.

Combining eq. (4) with eq. (1) leads to the following expression:

$$\frac{1}{\lambda F_w} = \frac{aRT}{V_w} \frac{1}{\Delta P} + \frac{bRT}{V_w} \quad (5)$$

This equation is identical to the empirical relationship suggested by Paul,<sup>14</sup> between the reciprocal of solvent flux and the reciprocal of pressure differential, for solvent permeation through swollen hydrogels. Paul undertook an extensive study of pressure and temperature dependence of water permeability through terephthalaldehyde-crosslinked PVA membranes<sup>14</sup> in order to verify a modified solution-diffusion model of solvent transport through a swollen, homogeneous hydrogel membrane. The reciprocal water permeability data determined by Paul in the pressure range 50–150 psi at 24°C are plotted vs. the reciprocal of pressure in Figure 8 along with data determined in this study at the same temperature in the pressure range 200–1000 psi. The good agreement between the two sets of data indicates that the linear relationship between the reciprocal of water permeability and the pressure differential is valid throughout the investigated pressure range 50–1000 psi. Accordingly, the extrapolation of these linear correlations to  $\Delta P = 0$  is valid.

The linear dependence between the reciprocal of the salt rejections and the reciprocal of the pressure differential at different salt concentrations (Fig. 7) is in good agreement with eq. (3). The slopes of these lines are proportional to the ratios between the salt permeability ( $P_s$ ) and water permeability ( $P_w$ ) of the membrane at the various feed concentrations. Since the water permeabilities of the membranes were found to be nearly independent of the feed salt concentrations, the increase in the slopes of the above-mentioned linear correlations with increasing feed concentration must be attributed to a strong dependence of the salt permeability on the feed concentration. The pronounced dependence of the salt rejection ( $R_s$ ) on feed concentration (Fig. 6) is also in agreement with

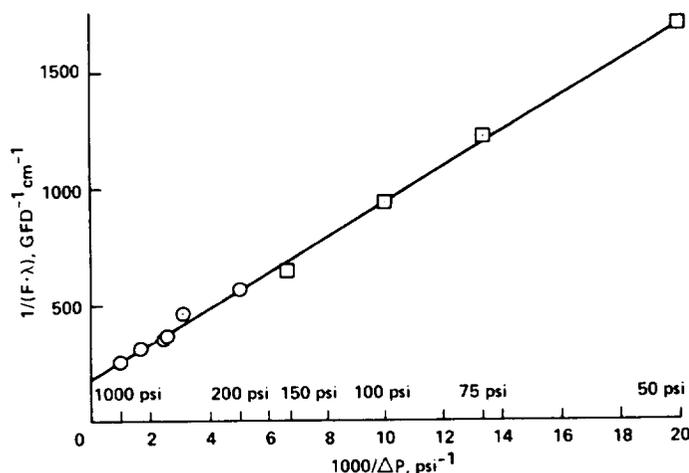


Fig. 8. Pressure dependence of water fluxes through PVA membranes as determined by Paul and Ebra-Lima<sup>13</sup> □, at 24°C,  $\lambda = 35 \mu\text{m}$ , see Fig. 2 of Ref. 13; and in this work ○, 90 GF 5 sample at 24°C,  $\lambda = 4.0 \mu\text{m}$  (●).

a feed concentration-dependent salt permeability coefficient. This dependence is reminiscent of a Donnan-type ion exclusion phenomenon. The problem is that this mechanism is characteristic of and limited to charged membranes. Even though in the case of radiation-crosslinked PVA it may be argued that ionic groups could be introduced as a result of the radiation treatment, in the case of untreated PVA membranes, where the same type of behavior was observed,<sup>15</sup> the presence of such charged groups seems very improbable.

The linear correlation between  $(R_s)^{-1}$  and  $(\Delta P)^{-1}$  shown in Figure 7 also indicates that the ratio between the salt permeability coefficients and the water permeability coefficient at a given feed concentration is independent of pressure. Since it has been shown previously that in these membranes  $(P_w)^{-1}$  is linearly dependent on  $\Delta P$ , the independence of  $P_s/P_w$  of  $\Delta P$  implies that the salt permeability coefficient of these membranes is subject to the same dependence on the pressure differential as the water permeability. This parallel pressure dependence of the water and salt permeability coefficients may be rationalized in terms of parallel variations in the water content (swelling) and salt content of the membranes, as a result of variations in the applied hydrostatic pressure.

The activation energies of  $P_w$  determined at the different pressures are shown in Table II along with the activation energies of the coefficients  $a$  and  $b$  derived from eq. (4). It is evident from this table that the activation energy for water permeability is independent of  $\Delta P$ , and this fact is further emphasized by the practical identity of the activation energies for  $a$  and  $b$ , with values confined within the range of  $6.05 \pm 0.11$  kcal/mol. This activation energy is overlapping the value of  $5.9 \pm 0.2$  kcal/mol reported by Peter and Mittelstadt<sup>16</sup> and is in reasonable agreement with the value of 6.5 kcal/mol reported by Paul.<sup>14</sup>

The identities of the temperature dependence of the observed water permeability and salt permeability of these membranes, as well as the relatively high values of these permeabilities, suggest coupled salt and water transport, in which case the similarity of the activation energies for salt and water permeation would be expected. The results reported by Thau et al.<sup>17</sup> suggest also that water permeation through PVA follows, at least in part, a pore flow mechanism, which could also provide an explanation for coupled transport. For such a case, however, the salt flux through the membrane would be composed of a diffusive contribution and a "coupled" contribution, dependent on the water flux. One would expect that the observed "effective" salt permeation coefficient in RO experiments would be larger than the purely diffusive salt permeation coefficient. Measurement of this diffusive salt permeability coefficient, which can be done in a system with no hydrostatic pressure differential across the membrane, indicated that this is not the case, however. Measurement of the salt permeability through a water-swollen untreated PVA membrane separating a 4 mM NaCl solution and distilled water, with no hydrostatic pressure applied at 25°C, yielded a salt permeability coefficient value of  $1.8 \times 10^{-6}$  cm<sup>2</sup>/s.\* The corresponding values, derived from the RO results obtained from experiments on the treated PVA membranes used in this study, are  $0.62 \times 10^{-6}$  cm<sup>2</sup>/s for the 90 GF 52 membrane and  $0.58 \times 10^{-6}$  cm<sup>2</sup>/s for the 80 GF 52 membrane.

Comparison of these values with the diffusive permeability (i.e.,  $1.8 \times 10^{-6}$  cm<sup>2</sup>/s) does not support the concept of coupled flow because, in such a case, the

\* M. G. Katz and T. Wydeven, "Selective Permeability of PVA Membranes. III. Diffusive Salt Permeability," manuscript in preparation.

opposite trend would be expected. The lower salt permeabilities probably reflect the fact that the water content of the radiation-crosslinked PVA membranes studied in these experiments was lower by a factor of 3 relative to the water-swollen untreated PVA (see Fig. 2). A parallel decrease in the salt distribution coefficient  $K$  in the radiation-crosslinked membranes may then explain their lower salt permeability. Thus, the salt transport data through water-swollen PVA hydrogels may be understood in terms of diffusive transport only, without the necessity of considering a contribution by "coupled" flow. This finding is consistent with the solution-diffusion model employed in the analysis of the results of this study.

### CONCLUSIONS

Both the water permeability and sodium chloride rejection of radiation-crosslinked PVA were comparable to those of untreated PVA.<sup>15</sup> While the water permeability of these membranes was considerably higher than that of chemically crosslinked PVA membranes,<sup>3-5</sup> the salt permeability was also very high, resulting in very poor salt rejection (20-50%). The main reason for the high salt permeability of these PVA membranes was probably due to the high water content which, even though smaller by a factor of  $\sim 3$  than that of the untreated PVA, is still higher by a factor of over 10 than that of formalized PVA membranes<sup>3</sup> and other efficient RO membrane materials such as cellulose and aromatic polyamides.

The high permeabilities and low rejections obtained are in agreement with the concept of a loose, open molecular structure for these radiation-crosslinked PVA membranes. Nevertheless, the results of this study indicate that the salt permeability of these membranes can be satisfactorily accounted for by purely diffusive transport.

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